

Gold nanoclusters as colloidal catalysts for oxidation of long chain aliphatic 1,2-diols in alcohol solvents

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Abstract

Long chain aliphatic 1,2-diols like 1,2-hexanediol and 1,2-octanediol can be converted to the corresponding α -hydroxy-alkanoates with total chemoselectivity, in an oxidation catalyzed by an aqueous gold sol under O₂ atmosphere. The sol is stabilized with poly(vinylalcohol), and the reaction is performed in alcohol solvents. Two methods are proposed for the efficient recycling of the colloidal Au catalyst. Firstly a solvent-resistant membrane filtration can be applied. As the membrane material, poly(dimethylsiloxane) is chosen. Secondly, in appropriate conditions, the reaction proceeds in the liquid biphasic mode, and the aqueous Au sol can be recycled by phase separation. Using either of both approaches, the colloidal stability and catalytic activity can be preserved over several recycles.

Keywords

1,2-diol, selective oxidation, gold nanoparticle, colloidal catalyst, solvent-resistant membrane filtration, biphasic catalysis.

Introduction

Application of gold is a young branch within catalytic science. For catalysis by zerovalent gold, it is increasingly clear that only small clusters exhibit sufficient catalytic activity (1). Owing to recently developed or improved synthesis methods, gold metal particles can be generated as nanoclusters. Gold metal catalysis therefore is truly a nanotechnology. Gold metal catalysis has already been successfully used in gas phase reactions like the low temperature oxidation of CO (2,3), the acetylene hydrochlorination (4), the water-gas shift (5) and the epoxidation of propylene (6). Examples of liquid phase metallic gold catalyzed reactions are redox reactions such as the oxidation of alcohols and aldehydes (7-9), the hydrogenation of unsaturated ketones to allylic alcohols (10) and the synthesis of H₂O₂ (11). Particularly in the liquid phase oxidation of 1,2-diols like 1,2-ethanediol and 1,2-propanediol, Prati and Rossi showed that gold is a suitable alternative for platinum group catalysts, because the surface of Au is not readily overoxidized and is hardly sensitive to chemical poisoning by acid adsorption (12). Gold catalysis moreover results in a high chemoselectivity to α -hydroxy-carboxylates and high conversions in a wide pH range.

While supported gold already received considerable attention in oxidation catalysis, the gold nanocolloids as such have seldomly been studied (13). Clearly, the application of a gold sol requires an appropriate catalyst recycling. The application of membrane filtrations is a relatively new approach to the recycling of dissolved catalysts (14), and in a preliminary report, we recently demonstrated that this method can be applied to the recuperation of catalytic Au nanocolloids, e.g. from aqueous reaction solutions (15).

In the present paper we focus on the oxidation of long aliphatic 1,2-diols, such as 1,2-hexanediol and 1,2-octanediol, applying a colloidal Au catalyst. As water is less suitable as a solvent for these substrates, alcohol solvents are used. Alcohols are preferred solvents for many oxidation reactions, even for large scale processes. In comparison with water, alcohols have some advantages: **1** – they dissolve a much broader range of organic compounds, **2** – they are easily separated from the products and recuperated via distillation, **3** – one avoids contamination of large volumes of water. Therefore, we investigate whether colloidal Au catalysts can be used in alcohol solvents. Two competing approaches for the catalyst recuperation will be compared, viz. membrane filtration and biphasic catalyst separation.

Experimental

Catalyst preparation

The synthesis of a pre-reduced Au sol catalyst is based on the methodology of Biella *et al.* (16). A standard aqueous Au/PVA sol catalyst was prepared by adding 1 ml of a 2.5 wt. % poly(vinylalcohol) solution (PVA, MW 13000-23000, 98% hydrolysed, Aldrich) to 100 ml of a stirred 0.002 M Au(III)-solution

($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$). Subsequent addition at 323 K, of 10 ml of a 0.4 M aqueous borohydride solution generates reduced gold nanoparticles (reduction time ≈ 60 s). The gold sols were characterized by UV-Vis absorption spectroscopy (Perkin Elmer Lambda 12) and transmission electron microscopy (Philips CM 20).

Membrane preparation

Poly(dimethylsiloxane) membranes were prepared according to Vankelecom *et al.* (17). This solvent-resistant membrane comprises a polyacrylonitrile/polyester support (VITO), coated by a poly(dimethylsiloxane) layer. The latter is prepared from the vinyl-functionalized prepolymer RTV 615A and the silicon hydride crosslinker RTV 615B (General Electric) dissolved in n-hexane in a 10:1 weight ratio. Variations in membrane preparation concerned the weight percentage of the prepolymer and crosslinker against the n-hexane volume; coating solutions with 5, 10, 15 and 20 wt% prepolymer were employed. This results in thicknesses of the PDMS top layer between 8 and 30 μm . As minor modifications to the reported procedure, the coating slope was changed from 90° to 30°, and as an adhesion promoter SS4155 (GE Bayer Silicones) was used (0.2 ml on 100 cm^2 of support surface).

Oxidation and catalyst recuperation experiments

Reactions were performed in following standard conditions, unless mentioned otherwise in the figure captions. A reaction mixture consists of 5 ml alcohol solvent, equimolar amounts of 1,2-diol and NaOH as the inorganic base (4 mmol each), and additionally a volume of the gold colloidal solution containing 1 μmol Au, resulting in a substrate/catalyst ratio (S/C) of 4000. This mixture was pressurized to 0.5 MPa O_2 and subsequently stirred and heated to 343 K during a standard reaction time of 6 h. The applied alcohol solvents were MeOH, $^i\text{PrOH}$ and $^t\text{BuOH}$.

For GC-analysis (CP-Sil-5, FID or MS detection), the reaction mixture was first acidified with HCl, and the reaction solvent was evaporated. After redissolution in a small volume of diethyl ether, the 1,2-diol substrates and the reaction products were derivatized by silylation of the hydroxyl functions using N-methyl-N-(trimethylsilyl)trifluoroacetamide (Avocado, >98%). Pure reference compounds for the products and the potential side products were silylated in the same way. The identity of the products was confirmed by GC-MS. Catalyst activity is expressed as the turnover frequency (TOF, h^{-1}), i.e. the molar ratio of the converted substrate over the catalyst, divided by the reaction time (h).

Membrane filtrations of diluted Au sols or reaction mixtures were performed at 298 K with a 0.5 MPa N_2 driving force. After the oxidation run, 5 ml of the reaction mixture was removed by membrane filtration, thus minimizing the volume containing the colloidal catalyst. In order to prevent contamination by residual reaction substrates and products, the gold sol volume was washed three times with the appropriate alcohol solvent; each time, a 0.5 ml volume was

retained in the membrane reactor. This allows to avoid errors in the GC analysis of consecutive oxidation runs. After this washing, fresh alcohol solvent, substrate and alkali base were added and a new oxidation run was started.

In order to investigate the Au retention by the membrane, and the membrane fouling by gold species, a membrane sample was taken after the gold sol filtration. After evaporation of the organic solvent, the sample was as such digested in *aqua regia*. Elemental analyses were then performed with ICP-AES (ICP-OES 3300DV). The detection limit of the technique (< 1 ppm for Au) is less than one thousandth of the total amount of gold present in the reaction mixture prior to filtration.

In case of the visibly biphasic reaction mixtures, the large alcoholic phase with 5 ml volume was removed by means of a pipette, leaving a small aqueous phase of about 0.5 ml containing the colloidal catalyst. Then 5 ml of the alcohol solvent, and 4 mmol of fresh 1,2-diol and inorganic base were added to the sol. As a control, the composition of this mixture was determined by GC analysis before reaction, in order to measure possible contamination by products of the previous run. Alternatively, different 1,2-diol substrates were used in consecutive runs. Such experiments indicated that contamination by products of a previous run can in practice be neglected.

Results and discussion

The standard synthesis of a PVA-protected Au sol, as used throughout this work, results in a sol with sufficient stability for reproducible oxidation reactions, e.g. of 1,2-propanediol in water (15). The physical properties of the aqueous sol were studied using absorption spectroscopy and electron microscopy, to obtain information about the gold dispersion and particulate dimensions. A maximum in the visible light absorption of the Au sol was observed at 539 nm (Figure 1). This band is ascribed to the surface plasmon resonance, and is conclusive evidence for the presence of zerovalent gold nanoparticles (18). The characteristic particle dimensions,

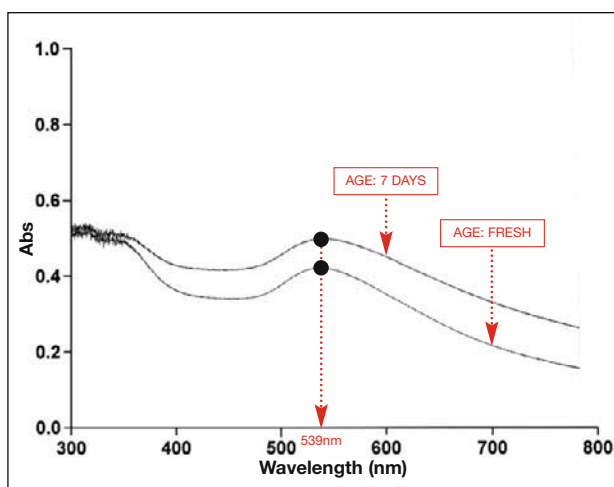


Figure 1

Visible light absorption spectra of a fresh and aged gold sol, both diluted in H_2O

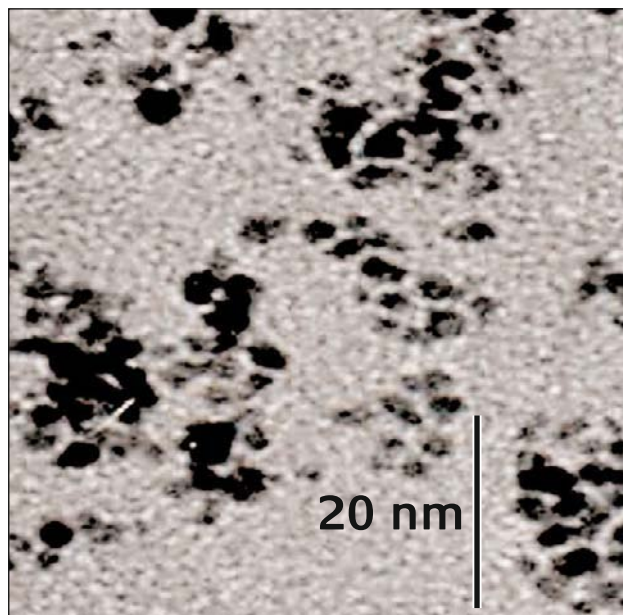


Figure 2
TEM visualization of a standard gold sol

determined by TEM, were 2-4 nm (Figure 2). Clearly the NaBH_4 excess results in a fast reduction of the gold cations, with the formation of small Au^0 nanoclusters as a consequence.

A main objective of our research was to investigate whether such Au sols are active catalysts in alcohol solvents. In the oxidation reactions, only a small amount of water is present (≈ 10 vol. %), which is introduced with the aqueous Au sol. When the oxidation was performed with the standard substrate and base concentrations, macroscopic inspection learned that the reaction mixture was visually homogeneous. In figure 3 the effect of the alcohol solvent on the 1,2-diol conversion is given, for both 1,2-hexanediol and 1,2-octanediol oxidation. Similar solvent effects were observed for both substrates. The TOF values in these alcohol solvents ($\leq 300 \text{ h}^{-1}$) are appreciably lower than e.g. for 1,2-propanediol oxidation in water, where values up to 850 h^{-1} have been observed (15). A possible explanation is based on the mechanistic proposal that the aldehyde

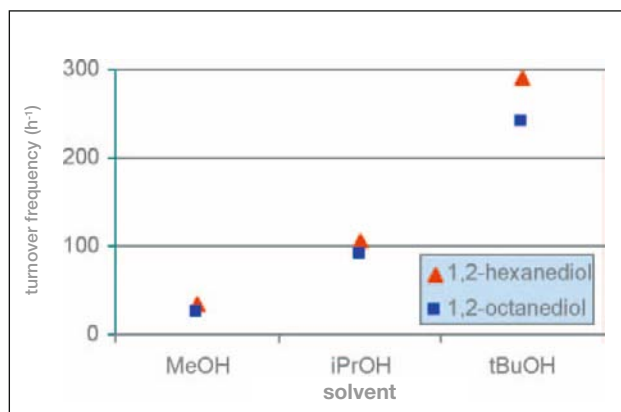


Figure 3
Effect of the alcohol solvent in the oxidation of 1,2-diol (standard conditions)

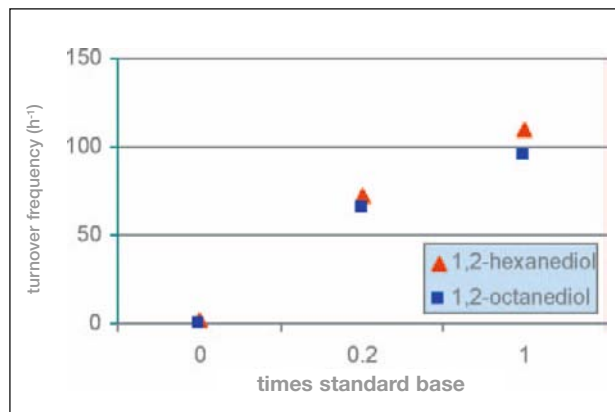


Figure 4
Effect of base promotion on the 1,2-diol oxidation in $i\text{PrOH}$ (standard conditions except for the amount of NaOH)

intermediate of the 1,2-diol oxidation is hydrated to a geminal diol before it is dehydrogenated to an acid. A low water concentration may therefore entail generally lower TOF values. A clear TOF increase is observed in going from primary to tertiary alcohol solvents: $\text{MeOH} < i\text{PrOH} < t\text{BuOH}$. Therefore, $i\text{PrOH}$ or $t\text{BuOH}$ were selected as a solvent for further experiments.

Next, the need for an inorganic base such as NaOH in the reaction was examined (Figure 4). Varying the amount of NaOH added to the reaction (0 – 0.2 – 1.0 equivalents) shows that the alkali base is clearly indispensable. The base may fulfill at least two roles. Firstly, the base may promote the dehydrogenation of the alcohol to the aldehyde by H^+ abstraction from the alcohol (19). Secondly, NaOH helps in desorbing the acid product from the metal surface by carboxylate formation.

Temperature has likewise a well-defined effect on the catalytic activity. As can be seen in Figure 5, an intermediate temperature of 343 K is most appropriate. The decreasing catalytic activity at higher temperatures is likely due to sol instability. After performing a 6h oxidation run at temperatures exceeding 353 K aggregation of the sol catalyst with formation of a dark-coloured deposit was observed. Between 323 and 343 K, the TOF shows only a

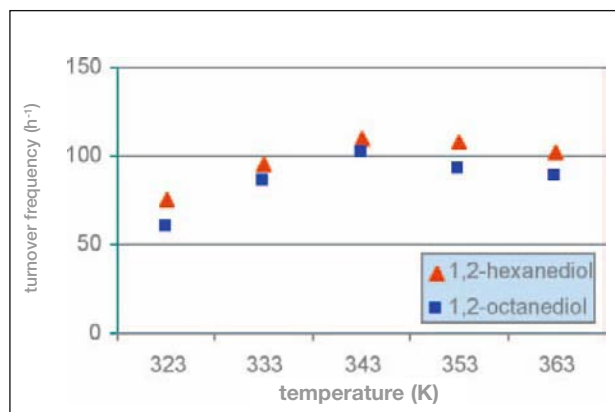


Figure 5
Effect of reaction temperature on the 1,2-diol oxidation in $i\text{PrOH}$ (standard conditions except for the reaction temperature)

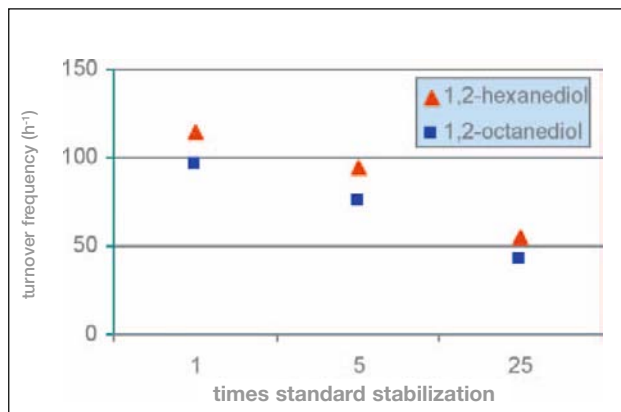


Figure 6

Effect of PVA concentration on the 1,2-diol oxidation in *i*PrOH (standard conditions except for the amount of PVA)

limited increase, which seems too small for the reaction to be purely under chemical control. In view of the high stability of the sols in these experiments, it seems unlikely that below 343 K considerable aggregation of the sols occurs. As a possible explanation, one may propose that diffusion of reagents to the PVA-enclosed Au colloids limits the turnover rate, which may explain the small apparent activation energy.

Figure 6 indeed demonstrates that an excess of PVA can decrease the turnover rate. When the amount of stabilizing agent in the sol synthesis is increased 25-fold, a 50% decline of the TOF is observed. This suggests that PVA can adsorb on the Au colloids and thus reduce the number of available active sites, or that diffusion of substrate molecules to the Au surface is hindered by the PVA chains surrounding the Au particles. Conversely, a too small amount of PVA stabilizing agent results in a quick deactivation due to Au particle aggregation. When the oxidation is performed with sols containing one fourth or less of the optimum PVA amount, the activity quickly decreases. Sols prepared with just one tenth of the standard PVA amount even were unstable, with immediate settling of Au aggregates.

In order to assess the longer term stability of the gold catalysts, the sols were aged during various periods before catalytic application. Therefore, the Au sol was diluted into the reaction solvent; the other compounds of the reaction mixture were added after a delay of 1, 7 or 28 days. Meanwhile, the diluted Au(0) solutions were kept at ambient conditions under atmospheric pressure. As is evident from the visible light absorption spectra of a fresh and an aged gold sol in Figure 1, the surface plasmon resonance band at 539 nm remains well preserved after 7 days, proving that the PVA satisfactorily stabilizes the gold dispersion. Catalytic data for the aged sols are given in Figure 7. At least 75% of the initial activity was maintained four weeks after sol synthesis, indicating that loss of catalytic activity by ageing is relatively minor.

In view of the satisfactory stability of the sol catalysts, the possibility of recycling the aqueous gold sol from the alcohol medium was examined. As a first possibility, filtration of the reaction mixtures by different PDMS membranes resulted in a

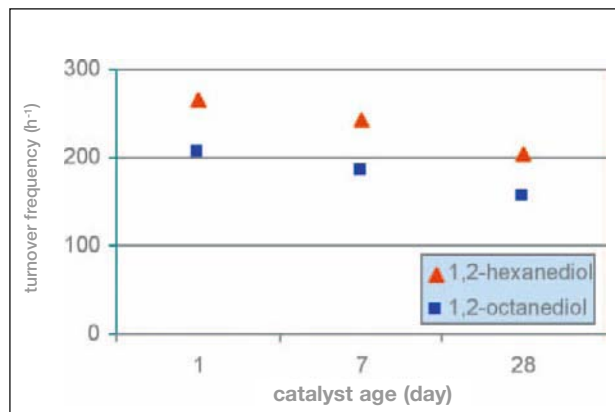


Figure 7

Effect of catalyst age on the catalytic activity for 1,2-diol oxidation in *t*BuOH (standard conditions)

total rejection of the catalytically active gold species. Moreover, fouling of the membrane, *i.e.* association of the Au/PVA colloids to the membrane material, was not observed. All PDMS membranes completely reject the gold colloids, while the other constituents of the mixture co-migrate with the alcohol solvent. Membranes with increasing thicknesses of the active PDMS layer were tested; this resulted in *t*BuOH fluxes varying from 2,240 l.(m²h)⁻¹ for the 5 wt% PDMS membrane (toplayer 8μm) to 0,630 l.(m²h)⁻¹ with the 20 wt% coated membrane (toplayer 30μm). The flux through the membrane is also affected by the nature of the alcohol solvent, which causes the membrane to swell to different extents. A linear relation between the membrane swelling and the membrane flux was found. The membrane swelling by *t*BuOH amounts to approximately 1,5 times the *i*PrOH induced swelling and as a result the *t*BuOH flux is about 1,5 times the *i*PrOH flux. In Figure 8 experimental data on the catalytic activity of recycled sol catalysts are reported. At least 80% of the inceptive sol activity was retained after three oxidation runs.

When the concentrations of 1,2-diol and base are increased twofold to 1.45 M, the Au sol is no longer well dispersed in the alcoholic medium, and phase separation occurs. The high electrolyte concentration is the probable

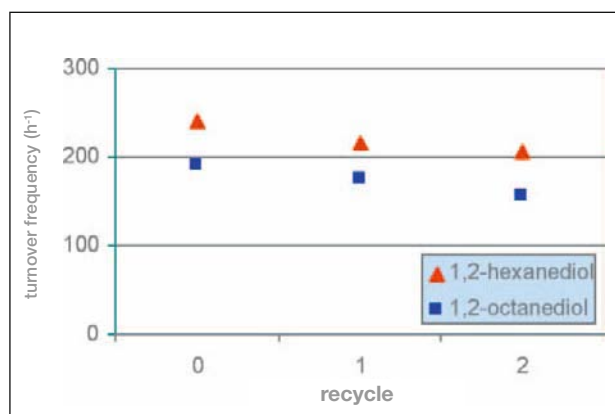


Figure 8

Recycling experiments in 1,2-diol oxidation in *t*BuOH by means of a membrane separation (standard conditions)

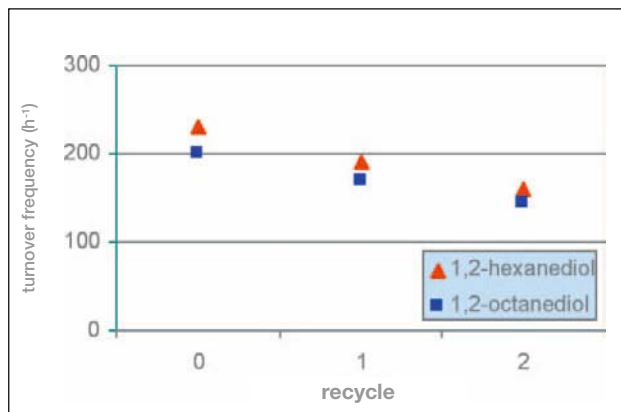


Figure 9

Recycling experiments in 1,2-diol oxidation in ^tBuOH by means of a phase separation (standard conditions, but 1,2-diol and NaOH concentrations are doubled)

cause of the phase separation. The volume of the aqueous phase is small, and, as found by analysis of the composition of the two phases, this volume contains the PVA-protected gold colloids and the inorganic base. The organic reagents are dissolved in the alcohol phase. As shown in Figure 9, the catalytic activities in the biphasic system are only slightly lower than in the pseudohomogeneous reaction. This proves that transport across the phase boundary is not a major rate limiting phenomenon. Recycling experiments were performed by removing the aqueous sol-containing layer and adding it to a fresh ^tBuOH solution of 1,2-diol and NaOH. As reported in Figure 9, about 70% of the initial activity was preserved after three consecutive runs.

Oxidations of 1,2-hexanediol and 1,2-octanediol in optimized conditions are reported in Figure 10. These conditions are: ^tBuOH as the solvent, 343 K, an equimolar amount of base and Au and additionally a Au : PVA ratio of ≈1000 on a molar basis. For both 1,2-diol oxidations, TON values exceeding 2000 are reached within 6 h, with maximum TOF values of 440 h⁻¹ and 360 h⁻¹ respectively for 1,2-hexanediol and 1,2-octanediol.

Finally, the oxidation of a few compounds related to 1,2-

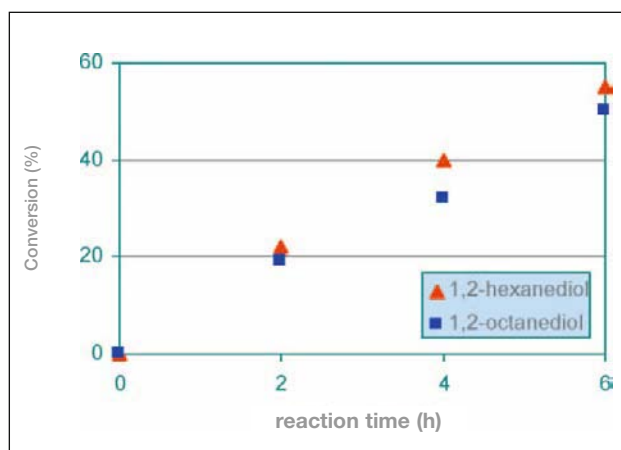


Figure 10

Conversion vs. time for the catalytic 1,2-diol oxidation with optimized catalyst and reaction parameters (^tBuOH, S/C 1000)

hexanediol was investigated, in order to assess a potential extension of the substrate scope. 1-hexanol and n-hexanal were selectively converted to Na-hexanoate, with turnover frequencies at 343K in ^tPrOH of respectively 25 h⁻¹ and 45 h⁻¹. Again, the chemoselectivity to the Na-alkanoate was complete; in the alkaline reaction conditions, no acetal or ester formation was observed. These values are considerably lower than observed for the 1,2-diols, indicating that the 1,2-diol moiety might play an important role in the substrate adsorption on the metal surface. The oxidation of the aldehyde is appreciably faster than the alcohol oxidation. This suggests that in the oxidation of the 1,2-diols, the initial step, viz. the oxidative dehydrogenation of the alcohol, is rate determining. This agrees with the observation that in the 1,2-diol oxidation, no reaction products other than the α-hydroxy-carboxylates are observed, pointing to the fast consecutive oxidation of the primary reaction products.

Conclusion

In this paper the feasibility of using well-stabilized gold sols as pseudohomogeneous catalysts has been demonstrated. Au sols emerge as active and chemoselective catalysts for the oxidation of aliphatic 1,2-diols. As the reaction can be conducted in alcohol media, with only a small volume of water, even long chain aliphatic 1,2-diols can be smoothly converted. Two approaches were compared to recycle the pseudo-homogeneous catalyst. Firstly, PDMS membrane filtration gives excellent preservation of activity, but a membrane reactor setup is required. Alternatively, at high solute concentrations, biphasic catalyst separation is possible, but the activity is less well preserved than with the membrane filtration. In optimized conditions, up to 2000 catalytic cycles can be performed per Au atom in the production of long chain α-hydroxy-alkanoates. The pseudohomogeneous Au sol catalysts appear to be a competitive alternative for heterogeneous metal catalysts in liquid phase oxidations.

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